

**Structural Studies of Microcrystalline Porphyrins**

K. Barkigia and M. Renner (BNL)

Beamline(s): X7B

**Introduction:** Porphyrins are tetrapyrrole derivatives that mediate a spectrum of bioenergetic reactions ranging from photosynthetic solar energy transduction to conversion of carbon dioxide into fuel. Their structures have been widely studied to ascertain the factors that control bioenergetic and catalytic reactions [1]. Recent applications include their use as sensitizers for photodynamic therapy (PDT) and in self-assembled arrays that are at the forefront of material science. Furthermore, oxidized metalloporphyrins are important intermediates in the catalytic cycles of heme proteins and in photosynthetic processes. In order to assess the stereochemical consequences of porphyrin oxidation, the structures of nonplanar model porphyrins that undergo one electron oxidation of the macrocycle to form cation radicals have been examined. Changes in conformation that occur upon oxidation have been shown to alter the chemical and physical properties of porphyrin complexes and may dictate their reactivity in vivo [2]. To address these diverse areas, we have recently determined the structures of several new porphyrins from microcrystals at beamline X7B. Among them are second-generation photosensitizers for PDT, polymeric assemblies and Co and Zn porphyrin radicals.

**Methods and Materials:** For each compound, at least two hemispheres of data were collected by the rotation method using a MAR345 image plate detector at liquid nitrogen temperature. The data were processed and merged with Denzo/Scalepack [3] and the structures were refined with the SHELXTL package [4].

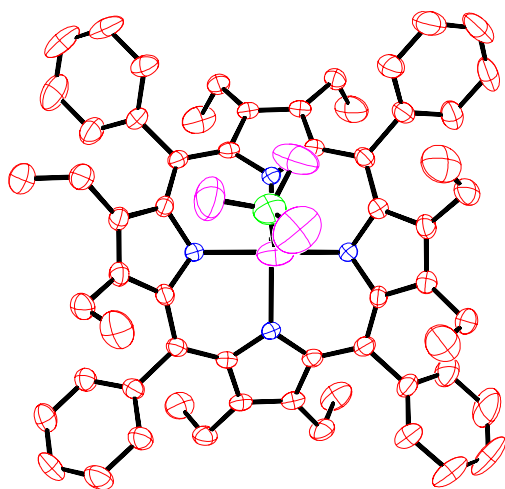
**Results:** One example of a sterically crowded Co porphyrin radical **1** is shown in Figure 1 and its distorted conformation is depicted in Figure 2. Derived esds on the Co-N and Co-O distances are 0.003Å. Final values of R1 and wR2 are 0.055 and 0.184 based on 5817 reflections [5]. The crystal measured 0.12x0.055x0.025 mm.

**Conclusions:** In general, the structures form the basis for calculations that serve to test theoretical treatments and to predict the properties of new porphyrins. Oxidation of a severely nonplanar Co(II) porphyrin to its cation radical **1** results in significant structural rearrangements.

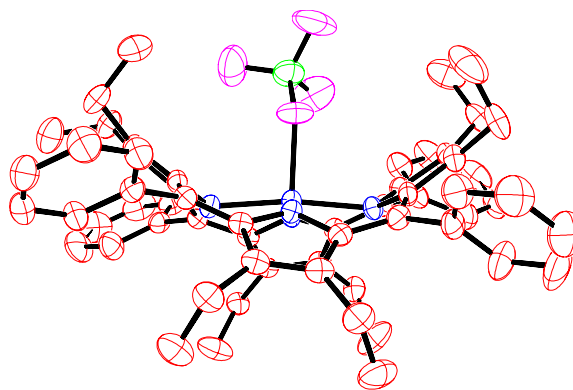
**Acknowledgments:** We thank Dr. Jonathan C. Hanson for assistance with the crystallographic data collection. The work at Brookhaven was supported by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC02-98CH10886.

**References:**

- 1 W.R. Scheidt, "Systematics of Porphyrins and Metalloporphyrins," *The Porphyrin Handbook*, p.49-112, 2000, K.M. Kadish, K.M. Smith, & R. Guilard, Eds., Academic Press.
- 2 J. Fajer, "Structural Effects in Chemistry and Biology. An Overview," *J. Porphyrins Phthalocyanines*, **4**, 382-385(2000) and references therein.
- 3 Z. Otwinowski and W. Minor, "Processing of X-ray Diffraction Data Collected in Oscillation Mode," *Methods in Enzymology*, Volume **276**: Macromolecular Crystallography, part A, p. 307-326, 1997, C. W. Carter, Jr. & R.M. Sweet, Eds., Academic Press.
- 4 G.M. Sheldrick, SHELXTL. Version 5.0. Siemens Analytical X-ray Instruments Inc. Madison, WI, USA, 1995.
- 5 K.M. Barkigia, M.W. Renner and J. Fajer, unpublished results.



**Figure 1.** Molecular structure of a Co porphyrin radical, **1**. Carbons are red, nitrogens blue, oxygens magenta and chlorine green. Hydrogens are omitted for clarity and the central Co(II)ion is hidden.



**Figure 2.** Edge-on view of **1**, which clearly illustrates the distorted conformation of the macrocycle and the perchlorate counterion that is bonded to the Co. Thermal ellipsoids are drawn at the 50% probability level in both figures.